Electrospining fabrication of nitrogen, phosphorus co-doped porous carbon nanofiber as electrochemiluminescent sensor for the determination of cyproheptadine

Regents

Polyacrylonitrile (PAN, Mw = 85,000 g mol^{-1}), polyvinylpyrrolidone (PVP, Mw = 54,000 g mol^{-1}), Ru(bpy)$_3$Cl$_2$·6H$_2$O, N, N-dimethylformamide (DMF), phosphoric acid and Nafion solutions (5 wt.%) were purchased from Sigma-Aldrich (Shanghai, China). Cyproheptadine hydrochloride was purchased from Shanghai yuanye Bio-Technology Co., Ltd (Shanghai, China). Cyproheptadine hydrochloride tablets was purchased from Guangdong Jiulianshan Pharmaceutical Co., Ltd (Guangdong, China).

Synthesis of N, P-PCNF

The spinning solution was prepared by stirring 1.2 g of PAN and 0.4 g of PVP added into DMF at room temperature for 12 h, then 0.16 g H$_3$PO$_4$ were added into the homogeneous solution and continue to stir for 12 h. The solution was placed into a 10 mL syringe and the parameters of electrospinning setup was set as follows: voltage, 18 kV; distance between tip and collector, 10 cm; flow rate, 2.0 mL h^{-1}; rotating speed, 180 rpm. The as-spun nanofibers were pre-oxidized at 280 °C for 2 h at a rate of 5 °C min^{-1} in air and then carbonized at 800°C for 2 h at the same rate in N$_2$. In the last, the

N, P-PCNF was obtained. For comparison, CNF was obtained by electrospinning PAN solution and porous carbon nanofiber (PCNF) was fabricated by electrospinning the mix solution of PAN and PVP.

Characterization

The morphology of P-PCNF was observed by Field-emission scanning electron microscope (FE-SEM; CarlZeiss, Germany). The elements composition analysis and chemical state of the material was investigated by X-ray photoelectron spectroscope (XPS, Kratos Analytical Ltd., UK). X-ray diffraction (XRD) was measured by on a Bruker D8A A25 X-ray diffractometer with Cu-Kα radiation ($\lambda=1.54178$ Å; voltage, 40kV; current, 40mA). Raman spectrum was obtained by XploRA PLUS (Horiba spectrometer). Nitrogen adsorption and desorption isotherms and the surface areas were characterized by Micromeritics ASAP 2460 using the the Brunauer–Emmett–Teller (BET) equation. The density functional theory (DFT) model was used to calculate the pore size distribution.

Fabrication of modified electrodes

Before modification, the glassy carbon electrode (GCE) must be polished by using 0.3 and 0.05 μm alumina slurries in turn, then ultrasonic cleaned in deionized water and ethanol alternately, and dried in N_2 lastly. The N, P-PCNF modified glassy carbon electrode (N, P-PCNF/GCE) was fabricated by dropping 1.5 mg·mL^{-1} of N, P-PCNF

powder suspension on the electrode and dried at room temperature. The PCNF modified electrode (PCNF/GCE) and CNF modified electrode (CNF/GCE) were prepared by the similar procedure as comparison.
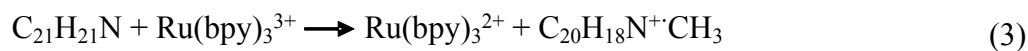
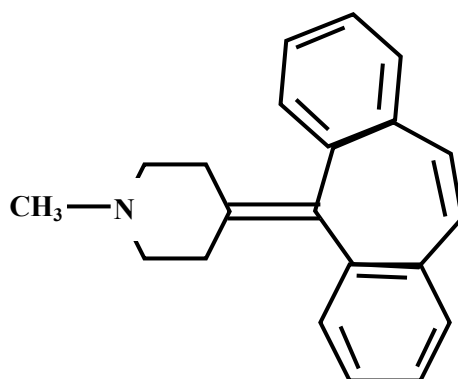**Electrochemical and electroluminescent measurements**

The electrochemical and electroluminescent measurements were performed on a MPI-E electrogenerated chemiluminescence analyzer (Xi'an Remex (Ruimai) Analysis Instruments Co., Ltd., Xi'an, China) in pH 7.5 phosphorus buffer solution (PBS) with a glassy carbon electrode (GCE, $\Phi = 3$ mm) as working electrode, a Pt wire as counter electrode, and Ag/AgCl as reference electrode under optimal conditions.

The electrochemical and ECL behavior of cyproheptadine

Fig. S1a and **S1b** exhibit that the CV curves and ECL curves of $Ru(bpy)_3^{2+}$, cyproheptadine and $Ru(bpy)_3^{2+}$- cyproheptadine system. The ECL intensity of $Ru(bpy)_3^{2+}$ is very weak suggesting a very low background, and the cyproheptadine shows no obvious ECL signal. However, the ECL intensity increases by 110 times after adding cyproheptadine into $Ru(bpy)_3^{2+}$ in **Fig. S1b**, which is due to that the reaction between tertiary amino of cyproheptadine and $Ru(bpy)_3^{2+}$ can produce higher ECL intensity. As depicted in **Fig. S1b**, the ECL intensity starts to increase sharply at around 0.9V and reaches maximum at about 1.0V, concurrent with the oxidation potential of $Ru(bpy)_3^{2+}$, which suggests that the oxidation of $Ru(bpy)_3^{2+}$ is of importance to the

process of ECL. In addition, the oxidation current of $Ru(bpy)_3^{2+}$ increases by the adding of cyproheptadine in the **Fig. S1b**, indicating that $Ru(bpy)_3^{2+}$ can catalyze the oxidation of cyproheptadine. The **Fig. S1c** and **S1d** demonstrate that the CV current and ECL intensity of $Ru(bpy)_3^{2+}$- cyproheptadine system on bare GCE, CNF/GCE, PCNF/GCE and N, P-PCNF/GCE. Obviously, the high current and ECL intensity of $Ru(bpy)_3^{2+}$- cyproheptadine system are acquired on N, P-PCNF/GCE, which is mainly attributed to that N, P-PCNF possess the large specific area for the more active sites and the high pore volume for the electron transfer. Based on the study of electrochemistry and ECL, the mechanism may be expressed as follows (1) to (7). Firstly, $Ru(bpy)_3^{2+}$ is oxidized to $Ru(bpy)_3^{3+}$ and cyproheptadine is oxidized to a cationic radical of short lifetime; next, a strong reducing and high energy intermediate is produced by deprotonation of the α-C of cationic radical; then, the intermediate reduces $Ru(bpy)_3^{2+}$ at the same time of energy transfer, forming a $[Ru(bpy)_3^{2+}]^*$ in excited state, which can emit light when it returns to ground state[1,2].

$$Ru(bpy)_3^{2+} - e^- \longrightarrow Ru(bpy)_3^{3+} \tag{1}$$

$$C_{20}H_{18}NCH_3 - e^- \longrightarrow C_{20}H_{18}N^{+\cdot}CH_3 \tag{2}$$

$$C_{21}H_{21}N + Ru(bpy)_3^{3+} \longrightarrow Ru(bpy)_3^{2+} + C_{20}H_{18}N^{+\cdot}CH_3 \tag{3}$$

$$C_{20}H_{18}N^{+\cdot}CH_3 \longrightarrow C_{20}H_{18}N^{\cdot}CH_2 + H^+ \tag{4}$$

$$C_{20}H_{18}N^{\cdot}CH_2 + Ru(bpy)_3^{3+} \longrightarrow [Ru(bpy)_3^{2+}]^* + C_{20}H_{18}N^+ = CH_2 \tag{5}$$

$$[Ru(bpy)_3^{2+}]^* \longrightarrow Ru(bpy)_3^{2+} + h\nu \tag{6}$$

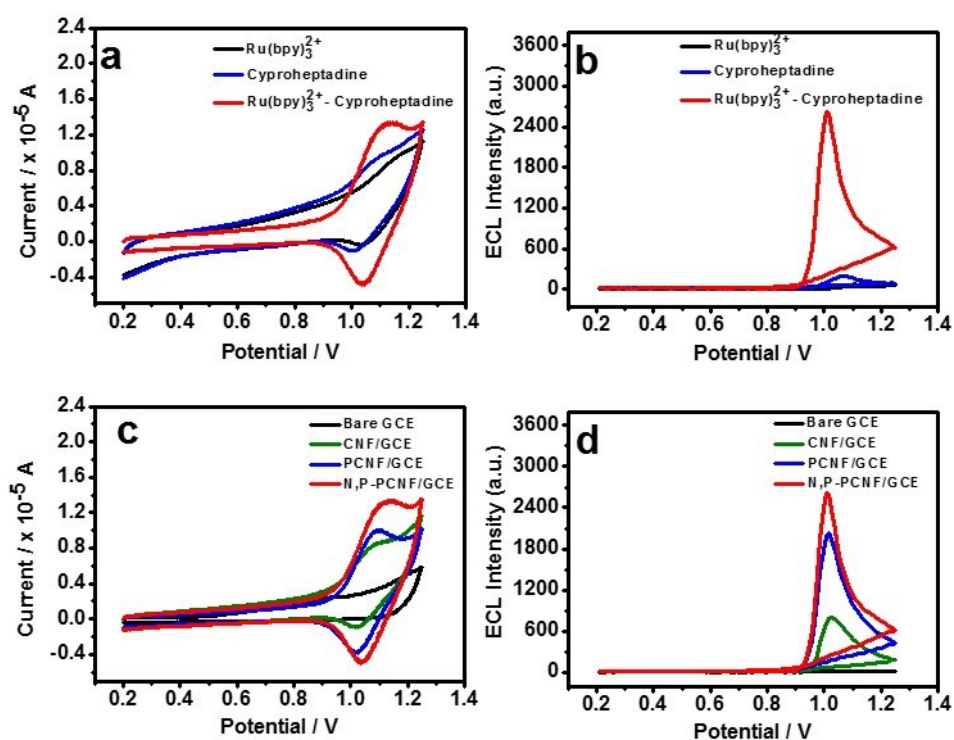**Scheme 1.** The structure of cyproheptadine

Figure S1. The cyclic voltammogram (CV) curves (a) and ECL curves (b) of $Ru(bpy)_3^{2+}$, cyproheptadine and $Ru(bpy)_3^{2+}$- cyproheptadine system in 0.1M pH 7.5 PBS. The CV curves (c) and ECL curves (d) of $Ru(bpy)_3^{2+}$- cyproheptadine system in 0.1M pH 7.5 PBS on different modified electrodes

References

1. Y. XueBo, S. BeiBei and H. XiWen, *SCIENCE IN CHINA SERIES B-CHEMISTRY*, 2009, **52**, 1394-1401.
2. J.-F. ZHANG, Z.-J. ZHANG, W. Yan, L. Yun-Yun and L. Ran, *Chinese Journal of Analytical Chemistry*, 2012, **40**, 730-734.